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CONDUCTIVE PASTE COMPOUND
[Dodensei Pesuto Soseibutsu]

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TITLE	(54):	CONDUCTIVE PASTE COMPOUND
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1. Title of the Invention

CONDUCTIVE PASTE COMPOUND

2. Claims

- (1) A conductive paste compound containing an additive comprised of a hydroxylated saturated or unsaturated higher fatty acid and a basic higher aliphatic amine and/or a nitrogenous heterocyclic compound for a conductive paste compound of copper powder and a synthetic resin.
- (2) A conductive paste compound wherein the hydroxylated saturated or unsaturated higher fatty acid additive claimed in Claim 1 is comprised of a hydroxystearic acid or ricinolic acid.
- (3) A conductive paste compound wherein the hydroxylated saturated or unsaturated higher fatty acid and the nitrogenous heterocyclic compound additives as claimed in Claim 1 are comprised of triethanolamine, N-cyclohexyldiethanolamine, di-n-octylamine, alkyltrioxyethylene ammonium hydroxide, N-n-butylldiethanolamine, 1,1,1**-nitro-2-propanol, quinoline and isoquinoline.

3. Detailed Explanation of the Invention

[Industrial Field of the Invention]

This invention relates to a conductive paste compound, in particular, a conductive paste compound containing copper powder.

* Numbers in the margin indicate pagination in the foreign text.

Along with the development of electronic equipment recently, there has been a move towards forming conductive circuits using screen printing with conductive paste compounds instead of forming conductive circuits by etching copper foil. There has also been a move towards the use of conductive paste compounds for attaching the binder connecting the conductors.

Since problems arise when electromagnetic waves generated by electronic equipment such as computers interfere with electrical waves, this problem has been resolved by applying conductive paste compounds to electromagnetic wave shields.

[Existing Art

Conductive paste compounds are composite materials of conductive fillers, binders made primarily of metallic powders and synthetic resins, and solvents or additives as necessary. The properties of the compound are determined by the properties of these substances and their combinations. /566

Presently, silver, copper and nickel powders are employed as the metallic powder and while silver and copper powders have excellent conductivity, silver powder is a precious metal so its value is very high. From a cost standpoint, copper powder is better but a surface oxide film develops very quickly so it is difficult to develop the conductivity. Nickel powder has less conductivity than copper powder. Also, the cost is generally higher than copper powder but lower than silver powder. A surface oxide film develops slower than with copper powder and the conductivity lasts longer.

As indicated above, even though copper powder is beneficial for conductivity from a cost standpoint and is often used as a substance

for a conductive compound, the rapid development of a non-conductive oxide film makes it difficult to handle in ambient conditions. Even when a conductive compound is produced using temporarily reduced copper powder, the electrical conductivity is lost when oxidation resumes. There have been many proposals to resolve this issue.

These methods employ various additives.

The additives include saturated and unsaturated higher fatty acids. Examples are given in Kokai58-61144, Kokai58-74759, Kokai58-145769, Kokai61-211738, Kokai62-230869, Kokai62-252988 and Kokai63-83178 and include palmitic acid, stearic acid, oleic acid and linolic acid. Reducing agents noted in the Kokai listed above include fatty acid amines, fatty acid phosphoric acid esters and metallic chelating agents. These include triethanolamine, dimethylamine and stearylamine. There are various ways to jointly use these.

[Problems this Invention is to Solve]

There are no satisfactory additives that eliminate oxidation of the copper powder.

This invention has the objective of presenting an additive that eliminates oxidation of copper by combining with one of various types of additives.

[Means of Solving these Problems]

The result of various investigations conducted by these inventors to solve these problems includes

- 1) A conductive paste compound containing an additive comprised of a hydroxylated saturated or unsaturated higher fatty acid and a basic higher aliphatic amine and/or a nitrogenous heterocyclic compound for a conductive paste compound of copper powder and a

synthetic resin.

2) A conductive paste compound wherein the hydroxylated saturated or unsaturated higher fatty acid additive claimed in Claim 1 is comprised of a hydroxystearic acid or ricinolic acid.

3) A conductive paste compound wherein the hydroxylated saturated or unsaturated higher fatty acid and the nitrogenous heterocyclic compound additives as claimed in Claim 1 are comprised of triethanolamine, N-cyclohexyldiethanolamine, di-n-octylamine, alkyltrioxyethylene ammonium hydroxide, N-n-butyldiethanolamine, 1,1,1**-nitro-2-propanol, quinoline and isoquinoline.

The copper powder employed in this invention can be a standard commercial product produced by electrolysis. The powder can take the form of slivers, granules or grains. While the diameter of the particles varies by application and is not specifically limited, diameters of 0.1-200 microns are recommended.

The resins employed in this invention include phenol resin, melamine resin and xylene resin. The phenol resin available commercially can be PC-1 produced by Mitsubishi Petroleum Chemicals (Corp.) or PL43488 produced by Gun Ei Chemicals (Corp.). The melamine resin can be Nikalac MX-708, MS-001 produced by Sanwa Chemicals (Corp.). The xylene resin can be PR-1540 produced by Mitsubishi Petroleum Chemicals (Corp.).

Examples of the hydroxylated saturated or unsaturated higher fatty acid include hydroxystearic acid or ricinolic acid (hereafter abbreviated as additive A).

Examples of the basic higher aliphatic amine and heterocyclic compound include triethanolamine, N-cyclohexyldiethanolamine,

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di-n-octylamine, alkyltrioxyethylene ammonium hydroxide, N-n-butyl-diethanolamine, 1,1,1-trinitro-2-propanol, quinoline and isoquinoline (hereafter abbreviated as additive A).

The ratio of copper powder for these copper paste compounds should be 75-95wt%, ideally 85-90wt%, with the balance being a resin for the binder and additives.

If outside of this range, the resistance increases.

The additives should be 0.5-10 parts by weight of acid to 100 parts by weight of copper powder, ideally 1-3 parts by weight, and 0.5-10 parts by weight of base, ideally 1-5 parts by weight.

If the amount added is too little, the resistance will increase. If the amount added is too much, the resistance will decrease, resulting in saturation, eliminating the need to add more, which may result in the loss of film strength.

[Embodiment Examples]

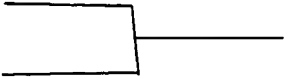
The following is a description of the embodiment examples in this invention.

Embodiment Example 1

Simple tests were conducted using ricinolic acid as additive A and triethanolamine as additive B.

1)

A copper paste (paste A) was produced containing additive A with the following amounts.

Copper powder	85g	
Resin	23.6g	
Additive A	2g	

Additive B was added with the following amounts.

Copper paste/additive B = 100/3 (wt. ratio)

2)

As shown in Fig. 1, copper foil was affixed to a plastic plate (a glass fiber reinforced epoxy resin laminate) with a width of 3cm and a length of 6cm. The copper foil in the center section 4 of the copper laminate was removed by etching. 1.5cm wide sections of copper foil 2 and 2 at both ends of the plastic plate 1 remained on the substrate A (with a gap of 3cm between the copper foil sections 2 and 2 at the ends of the substrate A). As shown in Fig. 2, conductive materials 1cm wide were applied to substrate A using a glass rod. The film 3 obtained (nearly 50 μ m after hardening) was cured for 15 minutes at 150°C and then the electrical resistance measured using a micrometer. The values were divided by 3 to obtain the area resistance. These results are shown as follows.

Additive A	Additive B	Area resistance (m Ω /□)
Yes	No	123
Yes	Yes	43
no	No	30x10 ⁹

There is a joint effect between the ricinolic acid and triethanolamine.

Embodiment Example 2

Each type of additive was tested using the following method.

Hydroxystearic acid and ricinolic acid were utilized as additive A while triethanolamine, N-cyclohexyldiethanolamine, N-n-butylldiethanolamine, 1,1,1**-nitro-2-propanol, quinoline and isoquinoline were utilized as additive B.

Amounts Added:

Copper powder	340g	} Paste A
Resin	95g	
Additive A	8g	
Paste A	50g	} A[]B[]
Additive B	1.5g	

50g of paste A were mixed with 1.5g of additive B.

Additives:

A-1: hydroxystearic acid

A-2: ricinolic acid

B-1: triethanolamine

B-2: nitrilopropanol (NTP)

B-3: N-cyclohexyldiethanolamine

B-4: butyldiethanolamine (BDEA)

B-5: xylene

B-6: isoquinoline

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Paste No.	Additives
	A B
A1B3	Hydroxy stearic acid/N-cyclohexyl diethanol amine
A2B5	Ricinolic acid/quinoline

B0 is a comparative example where there is no B element added.

Printing Conditions

Teflon 180 mesh emulsion thickness 15 μ

Using screen printing, the application area on the paper phenol (FR-2) and glass-epoxy substrate (FR-4) included three sizes as follows.

Sample Large: 2x2cm
 Medium: 1x1cm
 Small: 0.5x0.5cm

Curing Conditions

150°C x 15 minutes, 170°C x 15 minutes

Items to Confirm

The initial area resistance, area resistance of the cured film (film thickness of 15-20 μ) after being boiled for 60 minutes (after boiled) and data after the cured product was subject to 5 minutes of thermal treatment at 260°C were obtained.

Results are as shown in Tables 1 and 2.

Table 1

	F R - 2				F R - 4							
	150 °C×15分	煮沸後	0 °C×15分	煮沸後	150 °C×15分	煮沸後	150 °C×15分	加熱後	170 °C×15分	煮沸後	170 °C×15分	加熱後
A1B2 大 中 小	158 Ω	297 Ω	235 Ω	244 Ω	64 Ω	102 Ω	73 Ω	53 Ω	60 Ω	75 Ω	52 Ω	51 Ω
	128 Ω	141 Ω	47 Ω	56 Ω	76 Ω	107 Ω	90 Ω	110 Ω	80 Ω	118 Ω	43 Ω	1.1 Ω
	118 Ω	138 Ω	30 Ω	35 Ω	69 Ω	89 Ω	75 Ω	855 Ω	60 Ω	100 Ω	33 Ω	114 Ω
A1B3 大 中 小	1.8 Ω	6.1 Ω	320 Ω	374 Ω	135 Ω	180 Ω	110 Ω	128 Ω	80 Ω	86 Ω	43 Ω	45 Ω
	2.4k Ω		590 Ω	570 Ω	125 Ω	125 Ω	110 Ω	192 Ω	110 Ω	110 Ω	43 Ω	41 Ω
	4.0 Ω	6.9 Ω	80 Ω	78 Ω	105 Ω	105 Ω	98 Ω	205 Ω	80 Ω	84 Ω	42 Ω	73 Ω
A1B4 大 中 小	4.9 Ω	13.8 Ω	1.7 Ω	3.08 Ω	253 Ω	495 Ω	335 Ω	1.53 Ω	130 Ω	151 Ω	60 Ω	155 Ω
	414 Ω	∞	12.2 Ω	17.3 Ω	290 Ω	495 Ω	287 Ω	537 Ω	102 Ω	131 Ω	50 Ω	115 Ω
	1.33 Ω	2.3 Ω	2.68 Ω	3.1 Ω	180 Ω	280 Ω	200 Ω	13.2 Ω	71 Ω	96 Ω	50 Ω	195 Ω
A1B5 大 中 小	216 Ω	315 Ω	94 Ω	105 Ω	105 Ω	171 Ω	87 Ω	149 Ω	110 Ω	145 Ω	150 Ω	220 Ω
	155 Ω	230 Ω	67 Ω	73 Ω	90 Ω	139 Ω	90 Ω	165 Ω	100 Ω	132 Ω	157 Ω	276 Ω
	215 Ω	292 Ω	124 Ω	140 Ω	110 Ω	150 Ω	95 Ω	458 Ω	78 Ω	101 Ω	140 Ω	266 Ω
A1B6 大 中 小	140 Ω	147 Ω	137 Ω	160 Ω	81 Ω	98 Ω	90 Ω	235 Ω	105 Ω	130 Ω	83 Ω	117 Ω
	135 Ω	147 Ω	148 Ω	175 Ω	81 Ω	95 Ω	83 Ω	186 Ω	110 Ω	125 Ω	93 Ω	135 Ω
	113 Ω	120 Ω	127 Ω	147 Ω	89 Ω	111 Ω	90 Ω	138 Ω	105 Ω	123 Ω	95 Ω	215 Ω
A1B0 (大中小平均)	15 Ω	24 Ω	2.7 Ω	3.5 Ω	4.5 Ω	2.5 Ω	716 Ω	1.3 Ω	4.5 Ω	5.3 Ω	1.3 Ω	2 Ω

Table 1

Key:

	FR-2			
	150°C x 15 minutes	After boiled	0°C x 15 minutes	After boiled
A1B2 Large				
Medium				
Small				
A1B3 Large				
Medium				
Small				
A1B4 Large				
Medium				
Small				
A1B5 Large				
Medium				
Small				
A1B6 Large				
Medium				
Small				
A1B0 Average of Large, Medium & Small				

	FR-4			
	150°C x 15 minutes	After boiled	150°C x 15 minutes	After heated
A1B2 Large				
Medium				
Small				
A1B3 Large				
Medium				
Small				
A1B4 Large				
Medium				
Small				
A1B5 Large				
Medium				
Small				
A1B6 Large				
Medium				
Small				
A1B0 Average of Large, Medium & Small				

	FR-4 continued			
	170°C x 15 minutes	After boiled	170°C x 15 minutes	After heated
A1B2 Large				
Medium				
Small				
A1B3 Large				
Medium				
Small				
A1B4 Large				
Medium				
Small				
A1B5 Large				
Medium				
Small				
A1B6 Large				
Medium				
Small				
A1B0 Average of Large, Medium & Small				

Table 2

	F R - 2				F R - 4							
	150 °C × 15分	煮沸後	170 °C × 15分	煮沸後	150 °C × 15分	煮沸後	150 °C × 15分	煮沸後	170 °C × 15	煮沸後	170 °C × 15分	煮沸後
A 2 B 2 大	12.9 Ω	40.2Ω	178m Ω	174mΩ	202m Ω	325mΩ	250m Ω	90m Ω	85m Ω	110mΩ	59m Ω	55m Ω
中	6.33 Ω	14.4Ω	190m Ω	188mΩ	219m Ω	359mΩ	270m Ω	1.36Ω	112m Ω	130mΩ	76m Ω	1.48Ω
小	5.43 Ω	44.8Ω	76m Ω	73m Ω	120m Ω	203mΩ	270m Ω	660mΩ	76m Ω	95m Ω	55m Ω	1.3 Ω
A 2 B 3 大	21MΩ	∞	6.3 Ω	8.14Ω	348m Ω	596mΩ	92m Ω	34m Ω	73m Ω	105mΩ	227m Ω	216m
中	23MΩ	*	98mΩ	456mΩ	310m Ω	380mΩ	76m Ω	34m Ω	79m Ω	100mΩ	126m Ω	80m
小	1.8M Ω	*	5.2Ω	6.61Ω	118m Ω	142mΩ	48m Ω	23m Ω	59m Ω	195mΩ	68m Ω	279m
A 2 B 4 大	3.3M Ω	20.5M	9.9Ω	14.5Ω	293m Ω	365mΩ	226m Ω	136mΩ	146m Ω	180mΩ	217m Ω	2.7Ω
中	3.0M Ω	19.5M	17.4Ω	33.5Ω	428m Ω	518mΩ	244m Ω	159mΩ	65m Ω	38m Ω	372m Ω	461mΩ
小	62.4 Ω	14.8M	780mΩ	878mΩ	150m Ω	173mΩ	140m Ω	203mΩ	60m Ω	73m Ω	155m Ω	1.75m
A 2 B 5 大	204m Ω	282mΩ	165m Ω	180mΩ	177m Ω	269mΩ	170m Ω	240mΩ	103m Ω	130mΩ	64m Ω	89m Ω
中	208m Ω	297mΩ	180m Ω	208mΩ	193m Ω	297mΩ	172m Ω	278mΩ	123m Ω	160mΩ	54m Ω	85m Ω
小	150m Ω	202mΩ	160m Ω	188mΩ	103m Ω	157mΩ	120m Ω	1.52Ω	112m Ω	158mΩ	34m Ω	63m Ω
A 2 B 6 大	125m Ω	155mΩ	115m Ω	128mΩ	90m Ω	104mΩ	101m Ω	133mΩ	90m Ω	115mΩ	90m Ω	125mΩ
中	132m Ω	160mΩ	138m Ω	160mΩ	98m Ω	123mΩ	92m Ω	130mΩ	38m Ω	56m Ω	100m Ω	145mΩ
小	79m Ω	92Ω	111m Ω	125mΩ	93m Ω	125mΩ	96m Ω	146mΩ	35m Ω	55m Ω	84m Ω	129mΩ
A 2 B 0 (大中小平均)	7Ω	19MΩ	512 Ω	511Ω	5.6M Ω	7M Ω	1.5 Ω	1.5Ω	5.6MΩ	73 Ω	1.5 Ω	10 Ω

Table 2

Key:

	FR-2			
	150°C x 15 minutes	After boiled	170°C x 15 minutes	After boiled
A2B2 Large				
Medium				
Small				
A2B3 Large				
Medium				
Small				
A2B4 Large				
Medium				
Small				
A2B5 Large				
Medium				
Small				
A2B6 Large				
Medium				
Small				
A2B0 Average of Large, Medium & Small				

	FR-4			
	150°C x 15 minutes	After boiled	150°C x 15 minutes	After boiled
A2B2 Large				
Medium				
Small				
A2B3 Large				
Medium				
Small				
A2B4 Large				
Medium				
Small				
A2B5 Large				
Medium				
Small				
A2B6 Large				
Medium				
Small				
A2B0 Average of Large, Medium & Small				

	FR-4 continued			
	170°C x 15 minutes	After boiled	170°C x 15 minutes	After boiled
A2B2 Large				
Medium				
Small				
A2B3 Large				
Medium				
Small				
A2B4 Large				
Medium				
Small				
A2B5 Large				
Medium				
Small				
A2B6 Large				
Medium				
Small				
A2B0 Average of Large, Medium & Small				

The hydroxylated saturated or unsaturated higher fatty acid and basic higher aliphatic amine and/or a nitrogenous heterocyclic compound have a combined effect.

[Effect of this Invention]

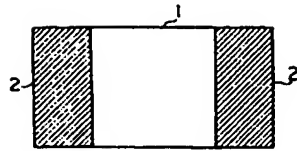
The additive in this invention has excellent conductivity and its effect as an additive enables it to be employed for all types of substrates.

4. Brief Description of the Figures

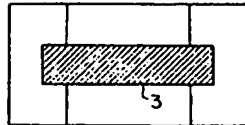
Figures 1 and 2 are front view drawings of the plastic plate for performing the abbreviated test for the conductive paste in this invention.

Figure 3 is a front view drawing of the conductive paste application on the paper-phenol and glass-epoxy plate to test the conductive paste in this invention.

[Figure 1]



[Figure 2]



[Figure 3]

